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(54) Laminated sheet.

(57) 7-Layer laminates comprising one layer of ethylene-vinyl alcohol copolymer, two adjacent layers of adhesive, two layers of a particular scrap regrind composition and two layers of polypropylene, the scrap composition comprising an inorganic mineral filler in an amount to prevent delamination between layers.

### LAMINATED SHEET

The present invention is concerned with laminated sheet made by coextrusion of layers of ethylene-vinyl alcohol copolymer (EVAL), adhesive, polypropylene and a reground blend of ethylene-vinyl alcohol copolymer, adhesive, polypropylene and inorganic mineral filler which disperses within the regrind. The laminated sheets can be used for the formation of articles such as plastic cups by methods comprising thermoforming, deep-drawing, solid phase forming, compression forming and the like.

Heretofore, in formation methods coextruded polyolefins sheets have been subject to problems of delamination or separation of the layers. Delamination has the adverse effects of a) unsightly defects, b) loss of part stiffness and c) loss of impact resistance. Typical, for example, is regrind which contains scrap of polypropylene, ethylene-vinyl alcohol copolymer and adhesive. Such regrind has materials of both high and low viscosity, which tend to separate when subjected to shear forces in a sheeting or film die. The ethylene-vinyl alcohol copolymer at high shear rates is of higher viscosity than the other components and tends to move towards the centre of the layer.

Multilayer sheet containing a layer of oxygen barrier polymer, such as EVAL, as well as layers of adhesive and polypropylene are commercially thermoformed into food containers for use in storing shelf stable oxygen sensitive foods. The unused web of sheet usually represents 30-50% of the sheet fed and is recovered for reuse. It has been found that this scrap upon regrinding and reextrusion forms a sheet which delaminates too readily upon flexing. This is believed to be due to a phase

separation of the incompatible EVAL and polypropylene in the high shear field inside the sheeting die.

The present invention provides for a regrind layer which comprises polypropylene or other polyolefins, ethylene-vinyl alcohol copolymer, adhesive and an amount of an inorganic mineral filler which will disperse within the regrind to give the coextruded sheet good lamination properties. Accordingly, the invention relates to a process for making a laminated sheet, comprising the steps of:

regrinding scrap sheet which contains polypropylene, ethylene-vinyl alcohol copolymer and adhesive;

adding to said scrap sheet regrind an inorganic mineral filler which will disperse with said regrind in an amount sufficient to prevent delamination between layers of said sheet from which said formed article is made;

coextruding said filler containing regrind with ethylene-vinyl alcohol copolymer, adhesive, and polypropylene into a 7-layer laminated sheet, the inner core thereof comprising ethylene-vinyl alcohol copolymer, the adjoining sub-core layers comprising adhesive and the inner and outer surface layers comprising polypropylene, respectively regrind composition or the same in reversed order.

In particular, the regrind layer comprises from 60 to 80 %wt of polypropylene, from 15 to 25 %wt of ethylene-vinyl alcohol copolymer, from 15 to 25 %wt of adhesive and 20 to 40 %wt of inorganic mineral filler, 100 %wt being the weight of the regrind layer.

The regrind layer composition is unique in that the inclusion of inorganic mineral filler, preferably calcium carbonate ( $\text{CaCO}_3$ ) or talc, works with the polypropylene, ethylene-vinyl alcohol copolymer and adhesive to prevent internal delamination in the regrind layer.

In preferred laminates, the ethylene-vinyl alcohol copolymer layer comprises from 0.5 to 25 %wt, the adhesive layer comprises from 0.5 to 15 %wt, the polypropylene layer comprises

from 25 to 95 %wt and the regrind layer comprises from 5 to 75 %wt, all weight percentages being calculated on the weight of the laminate. In the most preferred laminates the ethylene-vinyl alcohol layer comprises preferably 5 to 15 %wt, the adhesive layer comprises preferably from 3 to 7 %wt adhesive, the polypropylene layer comprises from 30 to 60 %wt and the regrind layer comprises from 50 to 95 %wt, all percentages by weight being calculated on the weight of the laminate.

The inorganic mineral filler should be selected among inorganic mineral fillers which will evenly disperse among the polypropylene, ethylene-vinyl alcohol, and adhesive of the regrind layer in order to give the present invention its unique properties.

The adhesive may be any suitable adhesive but is preferably selected from the group of EVA's, ionomers, thermoplastic rubbers such as KRATON<sup>®</sup>, available from Shell Chemical Company, Houston, Texas and, preferably, polypropylenes or polyethylenes modified with polar compounds such as maleic anhydride or acrylic acid.

Coextrusion technology to produce the laminates of the invention is known to those skilled in the art, one method employs 4 separate, annular concentric extrusion dies (blow extrusion) and flattening of the 4 tubular films so obtained. Alternatively straight slit extrusion, followed by adhering one laminate layer to the other one may be employed as well.

Example 1 (for comparison)

As shown in Table 1 below, a scrap control was prepared from dry blended 64% by weight commercial polypropylene (Grade 5524 sold by Shell Chemical Co, Houston, Texas), 18 %wt ethylene-vinyl alcohol copolymer (EVAL<sup>®</sup> E, from Kuraray of Japan) and 18 %wt Plexar 2110 adhesive, from Chemplex Co., USA. Each of these was dry tumbled at 150 rpm as pellets and the pellets were mixed with a one stage mixing screw. It will be

seen in Table 1 that the expected undesirable delamination occurred when the blend was converted into sheet by conventional sheet extrusion onto a three roll cooling stack.

TABLE 1  
COMPOSITION OF SCRAP CONTROL

<u>% , by weight</u>	<u>Composition</u>	<u>Free of Delamination</u>
64	PP 5524	
18	EVAL E	No
18	PLEXAR 2110	

Example 2

5        Table 2 shows the compositions of various scrap blends and  
delamination test results which were prepared in accordance with  
the above method. Each of the formulations in Table 2 represent  
potential compatiblizers which were dry blended with the scrap  
and transformed into sheet by extension. Formulation No. 1  
10       contained  $\text{CaCO}_3$ . Formulation Nos. 2-8 did not contain any  $\text{CaCO}_3$ .  
Formulation No. 1 contains 62 %wt of the scrap referred to in  
Example 1, 38 %wt WBS 139, from Shell Chemical Co., Houston,  
Texas. WBS 139 contains 80 %wt  $\text{CaCO}_3$  and 20 %wt of polybutene-1.  
Formulation No. 1 was free of delamination.

15       All of formulations Nos. 2-5 delaminated. PB 8010 is  
commercial polybutene-1, grade 8010, sold by Shell Chemical Co.,  
Houston, Texas.

TABLE 2  
DELAMINATION OF PARTICULAR SCRAP BLENDS

<u>FORMULATION NUMBER</u>	<u>COMPOSITION</u>	<u>%, BY WEIGHT</u>	<u>FREE OF DELAMINATION</u>
1	Scrap	62	
	WBS 139	38	YES
2*	Scrap	80	
	KRATON GX 2705	20	NO
3*	Scrap	85	
	KRATON DX 1300	15	NO
4*	Scrap	85	
5*	KRATON GX 1855	15	NO

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\* for comparison

### Example 3

Scrap blends containing various amounts of  $\text{CaCO}_3$  were tested for delamination. Compositions ranged from 0% by weight  $\text{CaCO}_3$  in control Formulation No. 1 to 40 %wt  $\text{CaCO}_3$  in Formulation No. 7. It may be noted from Table 3 that delamination occurred up to, and including, Formulation No. 4, which formulation contained 15 %wt  $\text{CaCO}_3$ . Formulation Nos. 5, 6 and 7 which contained 20 %wt, 20 %wt and 40 %wt  $\text{CaCO}_3$ , respectively, were free of delamination, however, indicating that an amount of  $\text{CaCO}_3$  of at least 20 %wt will prevent delamination. Multiflex<sup>®</sup>  $\text{CaCO}_3$ , made by Pfizer, is a different grade of calcium carbonate which consists of finer particle size.

TABLE 3  
DELAMINATION OF SCRAP BLENDS CONTAINING CaCO<sub>3</sub>

<u>NUMBER</u>	<u>COMPOSITION</u>	<u>%, BY WEIGHT</u>	<u>% BY WEIGHT CaCO<sub>3</sub></u>	<u>FREE OF DELAMINATION</u>
1')	PP 5524	64.0		
	EVAL E	18.0		
	PLEXAR 2110	18.0	0.0	NO
2')	Scrap	93.7		
	*WBS 139	6.3	5.0	NO
3')	Scrap	87.5		
	WBS 139	12.5	10.0	NO
4')	Scrap	81.0		
	WBS 139	19.0	15.0	NO
5	Scrap	75.0		
	WBS 139	25.0	20.0	YES
6	Scrap	50.0		
	Multiflex <sup>®</sup> CaCO <sub>3</sub>	50.0	20.0	YES
7	Scrap	50.0		
	WBS 139	50.0	40.0	YES

\* WBS 139 = 20% Polybutene-1, 80% CaCO<sub>3</sub>  
 ') for comparison

Example 4

Table 4, below, reveals delamination tests of scrap blends comprising talc as inorganic mineral filler. Formulation 1 is a dry blend of 50 %wt scrap (74% polypropylene 5524, 18% Plexar<sup>®</sup> and 18% EVAL<sup>®</sup>), 30 %wt of polypropylene and 20 %wt of talc.

TABLE 4DELAMINATION OF SCRAP BLENDS CONTAINING TALC

<u>COMPOSITION</u>	<u>FREE OF DELAMINATION</u>
Scrap/PP	
20 %wt talc	YES
EVAL/PP	
20 %wt talc	YES



C L A I M S

1. A process for making a laminated sheet, comprising the steps of:

regrinding scrap sheet which contains polypropylene, ethylene-vinyl alcohol copolymer and adhesive;

5 adding to said scrap sheet regrind an inorganic mineral filler which will disperse with said regrind in an amount sufficient to prevent delamination between layers of said sheet from which said formed article is made;

10 coextruding said filler containing regrind with ethylene-vinyl alcohol copolymer, adhesive, and polypropylene into a 7-layer laminated sheet, the inner core thereof comprising ethylene-vinyl alcohol copolymer, the adjoining sub-core layers comprising adhesive and the inner and outer surface layers comprising polypropylene, respectively regrind composition or  
15 the same in reversed order.

2. A process as claimed in claim 1 in which the regrind composition comprises from 60 to 80 %wt polypropylene, from 15 to 25 %wt ethylene-vinyl alcohol copolymer, from 15 to 25 %wt adhesive, and from 20 to 40 %wt inorganic mineral filler.

20 3. A process as claimed in claim 1 or 2, in which the adhesive is selected from ethylene-vinyl alcohol copolymer, ionomers, thermoplastic rubbers, and polypropylenes and polyethylenes modified with polar compounds such as maleic anhydride.

4. A process as claimed in any of claim 1 to 3, in which the  
25 inorganic mineral filler is  $\text{CaCO}_3$  or talc.

5. A method for making a formed article which comprises thermoforming, deepdrawing, solid-phase forming, or compression forming of a laminated sheet produced by a process as claimed in claims 1 to 4.

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54 Laminated sheet.

57 7-Layer laminates comprising one layer of ethylene-vinyl alcohol copolymer, two adjacent layers of adhesive, two layers of a particular scrap regrind composition and two layers of polypropylene, the scrap composition comprising an inorganic mineral filler in an amount to prevent delamination between layers.

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# EUROPEAN SEARCH REPORT

0161035  
Application number

EP 85 20 0686

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	FR-A-2 361 223 (TOYO SEIKAN KAISHA) * Claims 1-3, 6, 7, 9-15; page 7, line 20 - page 9, line 29; page 10, line 14 - page 12, line 36; examples 1, 7 *	1-3, 5	B 32 B 27/20 C 08 J 11/06
A	EP-A-0 000 558 (BASF) * Claim 1; page 2, line 30 - page 5, line 24; page 6, lines 10-12; page 7, lines 10-17; page 8, line 5 - page 10, line 12 *	1-5	
A	EP-A-0 084 922 (AMERICAN CAN CO.) * Claims 1, 2, 4-7, 10, 11; page 9, line 3 - page 13, line 4 *	1, 3, 4	
A	DE-A-2 144 536 (P. LAMORT et al.) * Claims 1, 3-5, 9, 11; page 2, paragraph 5 - page 4, paragraph 2 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			B 32 B C 08 J
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 21-04-1986	Examiner BLASBAND I.

## CATEGORY OF CITED DOCUMENTS

- X : particularly relevant if taken alone  
Y : particularly relevant if combined with another document of the same category  
A : technological background  
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E : earlier patent document, but published on or after the filing date  
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